Magnetic Annealing of Pt-alloy Nanostructured Thin Film Catalysts for Enhanced Activity

Project ID: FC121

David A. Cullen

Materials Science and Technology Division
Oak Ridge National Laboratory

2015 DOE Hydrogen and Fuel Cells Program Review

June 8, 2015

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
Overview

Timeline
Project Start: 10/1/2014
Project End: 9/30/2015

Barriers
Durability
Cost
Performance

Budget
Total DOE Funding: $300k
ORNL: $210k
NREL: $90k

Partners/Collaborators
ORNL: Orlando Rios, Craig Bridges, Harry Meyer III, Khorgolkhuu Odbadrakh
NREL: Shyam Kocha, Jason Zack
3M Company: Andy Steinbach, Dennis van der Vliet
Objective-Relevance

• Explore the potential of high magnetic field annealing to produce highly active surface structures in Pt-alloy oxygen reduction reaction (ORR) catalysts
  – Grain alignment
  – Modification of surface composition
  – Formation of new crystal structures

• Pt$_3$Ni$_7$ NSTF as a test structure
  – Ferromagnetic
  – Thin-film like structure
  – High specific activity
  – Further activity gains observed by transformation from nano- to meso-structure

Background: Magnetic Annealing

• High Field Magnetic Processing
  – 9T fields produced by superconducting magnets
  – Enables quenching, crystallization, annealing, sintering, compacting, extruding, sonicating at high temperature and field.

• Potential Impacts
  – Particle/grain alignment
  – Facilitate phase transformations
  – More homogeneous microstructures
  – Create new structures/compositions

Crystallizing ferromagnetic alloy in a magnetic field changes grain morphology (SEM).

Processing steel in a 9 Tesla magnetic field minimizes retained austenite.
Background: ORNL Houses World-Class R&D Magnetic Processing Facility

- 5” and 8” diameter bore magnets
- Vertical and horizontal geometries
- 9-inch long uniform field zone
- 0 to 9T magnetic field capability
- Operating temperatures 0°C - 2200°C
- Technology is centered around scalability and energy efficiency
Approach - High Magnetic Field Annealing

Materials Synthesis
- As-grown Pt$_3$Ni$_7$ provided by 3M
- In-house sputtered layers of varying compositions

Annealing in high magnetic field
- Performed on NSTF growth substrate
- Different temperatures and gas environments (H$_2$, Ar, etc.)

Characterization
- Rotating Disk Electrode (RDE)
- X-ray Photoelectron Spectroscopy (XPS)
- X-ray Diffraction (XRD)
- Transmission Electron Microscopy (TEM)

DFT Modeling
- Multiple Scattering Theory
## Approach - Milestones

<table>
<thead>
<tr>
<th>Task #</th>
<th>Project Milestones</th>
<th>Type</th>
<th>Task Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Demonstrate magnetic annealing on Pt3Ni7 NSTF-supported catalyst</td>
<td>Quarterly Progress Measure (Regular)</td>
<td>12/31/14</td>
</tr>
<tr>
<td>2</td>
<td>RDE testing demonstrating impact of magnetic annealing on mass/specific activity</td>
<td>Quarterly Progress Measure (Regular)</td>
<td>3/31/15</td>
</tr>
<tr>
<td>3</td>
<td>DFT modeling/microstructural characterization identifying modified morphologies responsible for activity changes</td>
<td>Quarterly Progress Measure (Regular)</td>
<td>6/30/15</td>
</tr>
<tr>
<td>4</td>
<td>Delivery of best-of-class catalyst via magnetic annealing with 1.5 times the mass activity of baseline.</td>
<td>Annual Milestone (Stretch)</td>
<td>9/30/15</td>
</tr>
</tbody>
</table>
Accomplishment 1: Magnetic Annealing NSTF Roll-good under 100% $H_2$

Typical heating curve

Pristine

200°C, Air

400°C, Air

400°C, $H_2$

Kapton® roll-good stable under Ar and $H_2$ at 400°C
Magnetic Annealing Experiments

Set 1
- Pristine Pt$_3$Ni$_7$ on growth substrate
- 100% Ar, 0T
- 100% Ar, 9T
- 100% H$_2$, 0T
- 100% H$_2$, 9T

400°C Anneal for 3hr

Set 2
- Pristine Pt$_3$Ni$_7$ on growth substrate
- 100% H$_2$, 9T, 240°C
- 100% H$_2$, 9T, 0 <-> 240°C

Set 3
- Pristine Pt$_3$Ni$_7$ removed from growth substrate
- 100% H$_2$, 0T, 400°C

• 3 sample sets produced thus far
• RDE performed on Set 1 and Set 3
Accomplishment 2: RDE Evaluation

- Standardized RDE Protocol
  - Electrolyte: 0.1 M HClO₄
  - Cell Temperature: Room Temp.
  - Break-in: 0.025 – 1.2 V, 0.5 V/s, 100 cycles, N₂
  - CV: 0.025 – 1.0 V, 0.02 V/s, 3 cycles, N₂
  - IV: −0.01 → 1.0 V, 0.02 V/s, 1600 rpm, O₂
Accomplishment 2: RDE Evaluation

- $\text{H}_2$ annealing provides superior activity to annealing in Ar
- Annealing in both Ar and $\text{H}_2$ leads to lower ECA and specific activity than as-grown material
  - Opposite trend of results published in literature on annealing NSTF in $\text{H}_2$
- Magnetic field yields higher ECA, lower specific activity
- Extended annealing of powder sample yields even lower activities
Accomplishment 3: XRD and XPS

Surface Composition (at.%)  

<table>
<thead>
<tr>
<th></th>
<th>Pt</th>
<th>Ni</th>
<th>O</th>
<th>C</th>
<th>Cr</th>
<th>N</th>
<th>Ni/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td>9.3</td>
<td>27.8</td>
<td>42.5</td>
<td>20.5</td>
<td>0.0</td>
<td>0.0</td>
<td>3.00</td>
</tr>
<tr>
<td>Ar_0T</td>
<td>10.5</td>
<td>12.8</td>
<td>10.0</td>
<td>63.7</td>
<td>0.2</td>
<td>2.8</td>
<td>1.22</td>
</tr>
<tr>
<td>Ar_9T</td>
<td>9.0</td>
<td>10.4</td>
<td>10.7</td>
<td>66.9</td>
<td>0.3</td>
<td>2.7</td>
<td>1.15</td>
</tr>
<tr>
<td>H2_0T</td>
<td>10.2</td>
<td>21.7</td>
<td>25.0</td>
<td>43.0</td>
<td>0.2</td>
<td>0.0</td>
<td>2.13</td>
</tr>
<tr>
<td>H2_9T_mid</td>
<td>10.4</td>
<td>21.5</td>
<td>21.8</td>
<td>45.8</td>
<td>0.5</td>
<td>tr</td>
<td>2.07</td>
</tr>
<tr>
<td>H2_9T_edge</td>
<td>11.7</td>
<td>27.5</td>
<td>25.0</td>
<td>35.8</td>
<td>0.0</td>
<td>0.0</td>
<td>2.34</td>
</tr>
</tbody>
</table>

- XPS shows C surface contamination after annealing (perylene-red sublimation)
- Difference in Ni/Pt between Ar and H2
- Grain size: As-grown -> Ar -> H2
- Magnetic field yields smaller grains with slightly larger lattice parameter

<table>
<thead>
<tr>
<th>Sample</th>
<th>Latt. par. (Å)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (lit.)</td>
<td>3.9231</td>
<td></td>
</tr>
<tr>
<td>As-grown</td>
<td>3.6977</td>
<td>3.8</td>
</tr>
<tr>
<td>Pt3Ni7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar 9T</td>
<td>3.6894</td>
<td>4.9</td>
</tr>
<tr>
<td>Ar 0T</td>
<td>3.6841</td>
<td>5.6</td>
</tr>
<tr>
<td>H2 9T</td>
<td>3.6779</td>
<td>5.9</td>
</tr>
<tr>
<td>H2 0T</td>
<td>3.6736</td>
<td>6.8</td>
</tr>
</tbody>
</table>
Accomplishment 4: STEM Analysis

As-grown  Ar, 0T  Ar, 9T  H₂, 0T  H₂, 9T  H₂, Powder

50 nm  50 nm  50 nm  50 nm  50 nm  100 nm
50 nm  50 nm  50 nm  50 nm  50 nm  100 nm
Accomplishment 4: STEM Analysis

- Increase in grain size with annealing confirmed in STEM
- No modification to surface structure/composition observed following magnetic annealing
Accomplishment 4: STEM Analysis

- Modification to surface structure/composition observed at 240°C, but not at 400°C
Accomplishment 5: SKKR-DFT Modeling

Outputs From First Principles Modeling

- Magnetic and electronic structures at ground state
- d-band shift
- Work function with respect to surface composition
- Energetics with respect to composition variations
- Stability with respect to surface/bulk composition
- Magnetic Phase Diagram
- Surface monolayer magnetism
- Magneto-crystalline anisotropy near the surface

- Screened Korringa-Kohn-Rostoker (SKKR) method better represents disordered systems
  - Coherent potential Approximation (CPA)
  - All Electron Method
  - Fully Relativistic - anisotropy
  - Spin-orbit coupling
Collaborations

• National Renewal Energy Laboratory (NREL)
  – Shyam Kocha (co-PI)
    • Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique (FC111)
  – Jason Zack
    • RDE testing

• 3M Company
  – Andy Steinbach
    • Supplier of Pt$_3$Ni$_7$ NSTF materials, helpful discussions on project findings and suggestions for future directions
  – Dennis van der Vliet
    • Guidance on H$_2$ annealing protocols, catalyst removal from growth substrate, and RDE testing of NSTF
Remaining Challenges and Future Work

• Improve magnetic response of NSTF material
  – Modify heating curves (time, max. temperature, etc.)
  – Generate new catalyst compositions (Pt$_{1-x}$Ni$_x$, Pt$_{1-x}$Co$_x$)
  – Measure magnetic properties via SQUID

• Characterize post-RDE catalysts
  – Break-in cycles modify composition/structure
  – XRD, XPS, and TEM characterization to be performed after RDE tests

• Durability tests
  – Observe effect of treatments on changes in mass activity, specific activity, and ECA over catalyst lifetime

• Input from Modeling Efforts
  – SKKR-DFT calculations to provide guidance on ideal catalyst compositions and surface structures

• Generate best-of-class catalyst with RDE-determined mass activity exceeding 1.3 A/mg$_{Pt}$
Summary

- **Relevance:**
  - Improve performance of alloy cathode catalysts through high field magnetic annealing

- **Approach:**
  - Study impact of magnetic annealing on Pt$_3$Ni$_7$ NSTF model structures, with characterization by RDE, XPS, XRD, and STEM

- **Accomplishments:**
  - Demonstrated magnetic annealing of Pt$_3$Ni$_7$ NSTF in a 9T field at 400$^\circ$C in Ar and H$_2$
  - Measured specific activity, electrochemical surface area, and mass activity by RDE
  - Characterized changes in grain size and surface composition using XPS, XRD, and STEM
  - Implemented SKKR method for advanced DFT calculations of disordered alloy catalysts

- **Collaborations**
  - Worked closely with NREL (RDE testing) and 3M (materials supplier, project guidance)

- **Future Work**
  - Modify catalyst compositions and annealing protocols to generate new high-performance structures.